Near-Field Polarimetric Characterization of Semi-Crystalline Polymer Systems

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INTRODUCTION

We have studied crystallization in thin films of isotactic polystyrene (iPS) to better understand the morphology and formation of these structures through the use of polarization modulation near-field scanning optical microscopy (PM-NSOM). Polymer crystallites consisting of ordered layers (lamella) of folded chains are grown from amorphous iPS film. While the structure of bulk polymer crystallites (spherulites) is well established,[1] a variety of less-understood forms, including dendritic structures, are found in ultra-thin (<100 nm) films.[2] In addition, there are questions regarding how crystallization occurs in these constrained systems where the film thickness is comparable to the polymer chain dimensions.

Thin films can be characterized by a variety of means. Ellipsometry and traditional polarimetry can be used to obtain the bulk (average) optical properties (e.g. dichroism, retardance) of thin films with high precision, but these methods do not provide a means to image micro- and/or nano- scale structures. Aperture near-field scanning optical microscopy (NSOM) provides a means for visible-light imaging with sub-diffraction limit lateral resolution, but the data are typically qualitative. By combining polarimetric techniques with NSOM, we can measure the local linear birefringence (retardance) and the linear dichroism of thin-film samples,[5-8] which provides quantitative information regarding molecular alignment in thin films with spatial resolution as high as 50 nm. NSOM-generated polarimetric images of polymer crystallites should provide valuable information regarding the mesoscopic morphology of these structures and give clues to their formation.

EXPERIMENTAL

Instrumentation. A detailed review of aperture transmission NSOM can be found in reference 3. Fiber probes are drawn from single mode optical fibers with apertures defined by an Al coating 200 nm thick. Aperture diameters range from 50 nm to 150 nm. The aperture is maintained at a distance of 5 nm to 10 nm from the sample surface using a shear force feedback loop.[4] The sample is scanned using a piezo-electric flexure stage. A polarization-modulation technique similar to that used by McDaniel and Hsu[5,6] was employed to measure birefringence and dichroism of the crystallites. Substantial improvements to this technique have been made to account for probe anisotropy (dichroism and birefringence) and permit separate determination of the fast and dichroic axis of the sample. In this study, linearly polarized light from the 488 nm line of an Argon ion laser passes through a photoelastic modulator (PEM) and quarter-wave retarder (QWR) such that the resulting light is linearly polarized with a polarization direction that oscillates at the PEM frequency (50 kHz) and with an angular amplitude determined by the depth of the PEM modulation. This light is coupled into the tail end of the fiber probe. To a first approximation, the birefringence of the fiber is nulled using a commercially available fiber polarization controller. Light transmitted from the NSOM aperture through the sample is collected with a photomultiplier tube and Fourier analyzed to obtain the DC, 50 kHz and 100 kHz intensity components. The local dichroism of the material can be obtained directly from these measurements. When a circular analyzer (QWR and linear polarizer) is placed after the sample, Fourier analysis of the transmitted signal yields components which are also sensitive to sample birefringence. *If the dichroism and residual birefringence (after nulling) of the aperture probe are correctly accounted for,* the local dichroism and birefringence of a sample can be determined through this modulation technique. More detailed description of this approach, in particular the means by which the aperture probe properties are measured and compensated for, can be found in Refs. 7 and 8.

Sample Preparation. The samples studied here are made from 600,000 molecular mass isotactic polystyrene, spun cast from toluene onto glass coverslips that have been treated with a hydrophobic self-assembled monolayer to prevent dewetting. The samples were dried under vacuum for two days and then crystallized at 160 ºC, with quenching after 1 hour to arrest further growth. The 2D spherulites (Fig. 1) were determined to have a film thickness of 60 nm, while the random dendrite samples had a thickness of 15 nm (Fig. 2).

RESULTS

Three sample types have been investigated so far. The first, shown in Fig. 1, consisted of small spherulites early in their growth. We show here images of the DC component of the transmitted light (a), the topography (b), the retardance (c), and the relative alignment of the fast axis (d). The retardance image clearly shows an ordered crystallite (high retardance) surrounded by amorphous PS (retardance near zero). Absolute values for the fast-axis orientation are impossible to obtain due to circular birefringence in the fiber probe, but relative values shown in (d) clearly illuminate defect structures near the center of the spherulite and seem also to show radially aligned strain, near the thin "depletion zone" at the spherulite periphery.
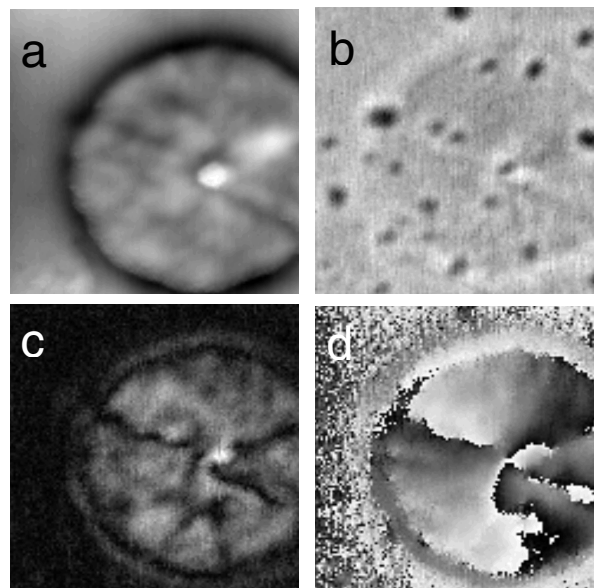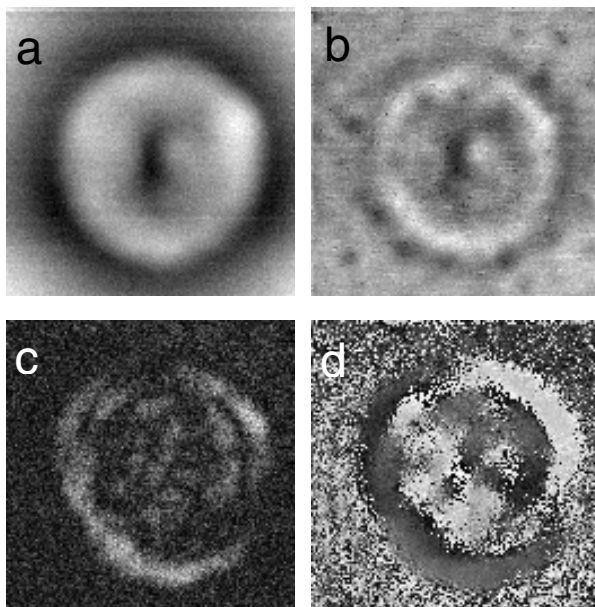

Figure 1. PM NSOM of an iPS spherulite. Images are 6 μm x 6 μm. (a) topography [0 nm to 40 nm], (b) transmission [0.2 to 0.25 (arbitrary units)], (c) retardance [0 mrad to 110 mrad], (d) relative alignment of the fast axis [0° to 180°].

Figure 2 shows an example of a dendritic crystallite in an otherwise amorphous 15 nm thick PS film. Here the order is less well established and a maximum retardance of 20 mrad is barely visible against the amorphous background. However, inspection of the retardance image (Fig. 2c) shows a faint, but discernible, outline of birefringent material outside the crystallite boundaries similar to that seen in Fig 1c.

Figure 3 shows an intermediate formation, where strain in the depletion zone around the crystallite seems to provide the largest birefringence, but the retardance is still overall less than that measured for the better developed spherulite shown in Fig. 1.
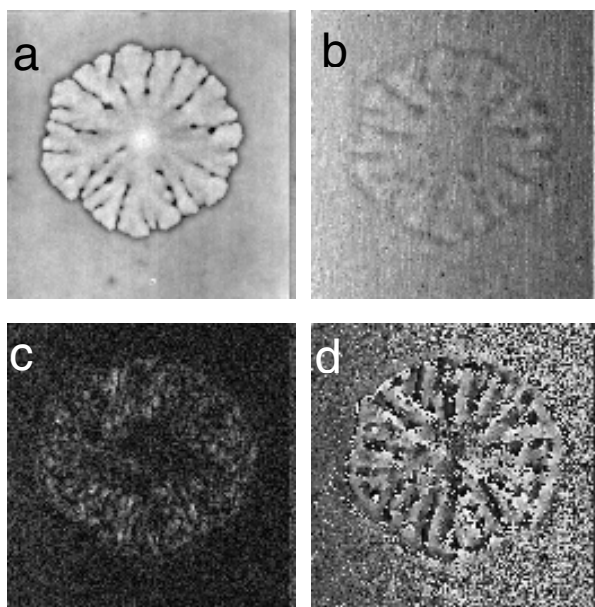
Figure 2. PM NSOM of a dendritic iPS crystallite. Images are 4.8 μm x 4.8 μm. (a) topography [0 nm to 15 nm], (b) transmission [0.16 to 0.20 (arbitrary units)], (c) retardance [0 mrad to 20 mrad], (d) relative alignment of the fast axis [0° to 180°].

Figure 3. PM NSOM of a iPS crystallite. Images are 3.66 μm x 3.66 μm. (a) topography [0 nm to 55 nm], (b) transmission [0.16 to 0.2 (arbitrary units)], (c) retardance [0 mrad to 50 mrad], (d) relative alignment of the fast axis [0° to 180°].

DISCUSSION

We have demonstrated the capability of PM-NSOM polarimetry to measure the local retardance of thin films with resolution of 10 mrad. Spatial resolution is between 50 nm and 150 nm. Our image data show evidence of a strained (and radially aligned) depletion zone at the periphery of the crystallites. These data directly suggest that polymer chains in the amorphous state become elongated before they are incorporated into the crystal – a new observation which has ramifications on how these thin structures are formed. Defect structures and amorphous regions within otherwise ordered crystallites are also imaged with ease. These observations will be discussed further as this new work progresses.

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